

# Brownian particle in ideal gas: explicit density expansions, conditional probabilities, and amusing properties of molecular chaos

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Explicit density expansions of non-equilibrium probability distribution functions for molecular Brownian particle in ideal gas are obtained in original form what visually implies (is exact solution to) the previously established dynamical virial relations. Role of these relations in unbiased analysis of molecular chaos properties in many-particle statistical mechanics, including the mobility  $1/f$  noise, is newly investigated in clear terms of conditional probabilities and averages.

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## I. INTRODUCTION

Here, we continue consideration of special but principally important problem of non-equilibrium statistical mechanics: factual statistics of random walk of molecular-size Brownian particle (BP) interacting with atoms of thermodynamically equilibrium ideal gas [1–4]. Namely, using a formal trick like suggested in our recent work [5], we shall derive explicit series expansions of the BP's and many-particle probability distribution functions over mean density of the gas. We shall see that these expansions, being represented in terms of the irreducible correlation (cumulant) functions, give unique formal solution to the exact “virial relations” [1–3, 6, 7] (if considered as equations for the correlation functions). Then we shall discuss some important consequences of these results, first of all, concerning existence of  $1/f$ -type BP's mobility fluctuations and essentially non-Gaussian long-range statistics of BP's path (dramatic failure of the “law of large numbers” in true many-particle statistical mechanics).

## II. DENSITY EXPANSION OF PROBABILITY DISTRIBUTION FUNCTIONS

Let  $N \gg 1$  ideal gas atoms are contained, along with the BP, in a box with volume  $\Omega = N/n \gtrsim a^3 N$  where  $n$  and  $a$  denote mean density of the gas (concentration of atoms) and characteristic radius of BP-atom interaction, respectively. The interaction potential,  $\Phi(\rho)$ , is assumed repulsive and short-range. Let at initial time moment,  $t = 0$ , full normalized  $(N + 1)$ -particle distribution function (DF) of this system is

$$D_N(t = 0) = F_0^{in}(R, V) \prod_{j=1}^N \frac{E(r_j - R) G_m(v_j)}{\int_{\Omega} E(r - R) d^3r} \quad (1)$$

Here  $R, V$  and  $r_j, v_j$  are coordinates and velocities of BP and atoms,  $F_0^{in} = F_0(t = 0)$  is BP's initial probability distribution (normalized to unit),

$G_m(v) = (2\pi T/m)^{-3/2} \exp(-mv^2/2T)$  is Maxwell velocity distribution for particle with mass  $m$ , and

$$E(\rho) = \exp[-\Phi(\rho)/T].$$

Clearly, if  $F_0^{in}(R, V) = W^{in}(R) G_M(V)$  (with  $M$  being BP's mass) then the distribution (1),  $D_N(t = 0) \propto W^{in}(R) \exp(-H^{(N)}/T)$  (with  $H^{(N)}$  being full system's Hamiltonian), represents thermodynamically equilibrium system, but it is not statistically equilibrium (stationary) because of its spatial inhomogeneity in respect to BP's position if described by more or less localized initial distribution  $W^{in}(R)$ , e.g.  $W^{in}(R) = \delta(R)$  (which will be taken in mind below).

At  $t > 0$ ,  $D_N(t) = \exp(L^{(N)}t) D_N(t = 0)$ , where  $L^{(N)}$  denotes full system's Liouville operator (corresponding to  $H^{(N)}$  and taking into account interactions with the box walls). For our system we can write

$$L^{(N)} = L_0 + \sum_{j=1}^N L_j, \quad (2)$$

where operator  $L_0$  represents BP itself, while operators  $L_j$  with  $j > 0$  represents  $j$ -th atom itself plus its mutual interaction with BP.

Further, introduce sequence of  $(s + 1)$ -particle ( $s = 0, 1, 2 \dots N$ ) marginal probability distribution functions (DF) for BP and  $s$  atoms:

$$\begin{aligned} F_s(t) &= \Omega^s \int_{s+1} \dots \int_N D_N(t) = \\ &= \Omega^s \int_{s+1} \dots \int_N e^{L^{(N)}t} D_N(t = 0), \end{aligned} \quad (3)$$

where  $\int_j$  symbolizes integration over variables of  $j$ -th atom. Thus, in respect to atoms' coordinates, these DF are “normalized to volume”, i.e. defined standardly, like in the mentioned references and originally by Bogolyubov in [8]. Consider them under the thermodynamic limit, - when  $N \rightarrow \infty$  and  $\Omega \rightarrow \infty$  (boundaries of the container disappear at infinity) under fixed  $N/\Omega = n = \text{const}$ , - as functions of the mean gas density  $n$ .

With this purpose, it is convenient, firstly, to introduce, like in [5], “coherent product”  $\circ$  of operator exponentials by definition as follows:

$$e^{A_1} \circ \dots \circ e^{A_s} \equiv e^{A_1 + \dots + A_s}$$

Then, secondly, to use identities

$$e^{L^{(N)}t} = e^{L_0t} \prod_{j=1}^N \circ[1 + (e^{L_jt} - 1)] = e^{L_0t} + e^{L_0t} \sum_{k=1}^N \sum_{1 \leq j_1 < \dots < j_k \leq N} \circ[e^{L_{j_1}t} - 1] \dots \circ[e^{L_{j_k}t} - 1] \quad (4)$$

and

$$\begin{aligned} e^{L^{(N)}t} &= e^{(L_0+L_1+\dots+L_s)t} \prod_{j=s+1}^N \circ[1 + (e^{L_jt} - 1)] = \\ &= e^{(L_0+L_1+\dots+L_s)t} \left\{ 1 + \sum_{k=1}^{N-s} \sum_{s+1 \leq j_1 < \dots < j_k \leq N} \circ[e^{L_{j_1}t} - 1] \dots \circ[e^{L_{j_k}t} - 1] \right\} \end{aligned} \quad (5)$$

Substituting this expansions to (3) we see that any finite-number term of corresponding series expansions of  $F_s(t)$  is well defined in the thermodynamic limit. Combining Eqs.1, 3 and 5, after quite obvious algebra, one obtains

$$F_0(t, R, V) = \mathbf{S}(t) F_0^{in}(R, V), \quad (6)$$

where the BP's "propagator"  $\mathbf{S}(t)$  is presented by series

$$\begin{aligned} \mathbf{S}(t) &= e^{L_0t} + e^{L_0t} \sum_{k=1}^{\infty} \frac{n^k}{k!} \prod_{j=1}^k \int_j \circ[e^{L_jt} - 1] g(x_j) = \\ &= e^{L_0t} + n \int_1 [e^{(L_0+L_1)t} - e^{L_0t}] g(x_1) + \\ &+ \frac{n^2}{2} \int_1 \int_2 [e^{(L_0+L_1+L_2)t} - e^{(L_0+L_1)t} - e^{(L_0+L_2)t} + e^{L_0t}] g(x_1) g(x_2) + \dots, \end{aligned} \quad (7)$$

with  $x_j \equiv \{\rho_j, v_j\}$ ,  $\rho_j \equiv r_j - R$ ,  $g(x) \equiv \exp[-\Phi(\rho)/T] G_m(v) = E(\rho) G_m(v)$ , and  $\int_j \dots = \int d^3\rho_j \int d^3v_j \dots$ .

At that, after change of variables from  $r_j$  to  $\rho_j = r_j - R$  and transition to the thermodynamic limit, the components of full Liouville operator (2) can be chosen as

$$L_0 = -V\nabla - f\nabla_P, \quad (8)$$

$$L_j = (V - v_j)\nabla_j + \Phi'(\rho_j)(\nabla_{p_j} - \nabla_P), \quad (9)$$

where  $\Phi'(\rho) = \partial\Phi(\rho)/\partial\rho$ ,  $\nabla = \partial/\partial R$ ,  $\nabla_j = \partial/\partial\rho_j$ ,  $\nabla_P = \partial/\partial P$ ,  $\nabla_{p_j} = \partial/\partial p_j$ ,  $P = MV$  and  $p_j = mv_j$  are momenta of BP and atoms, and we introduced external force  $f$  acting onto BP.

Notice that  $k$ -th term of (7) represents all such BP's trajectories what include  $\geq k$  collisions with  $k$  atoms, at least one collision with any of them. Indeed, if BP was not interacting with  $j$ -th of them, i.e.  $L_j$  was replaced by  $(V - v_j)\nabla_j$ , then integration  $\int_j$  would turn into zero any whole  $k$ -th term of (7) with  $k \geq j$ .

Similarly, from Eqs.1, 3 and 5 it follows that

$$\begin{aligned} F_s(t) &= e^{(L_0+L_1+\dots+L_s)t} \left\{ 1 + \sum_{k=1}^{\infty} \frac{n^k}{k!} \prod_{j=s+1}^{s+k} \int_j \circ[e^{L_jt} - 1] g(x_j) \right\} F_0^{in} \prod_{j=1}^s g(x_j) = \\ &= e^{(L_0+L_1+\dots+L_s)t} F_s^{in} + e^{(L_0+L_1+\dots+L_s)t} \sum_{k=1}^{\infty} \frac{n^k}{k!} \left\{ \prod_{j=s+1}^{s+k} \int_j \circ[e^{L_jt} - 1] \right\} F_{s+k}^{in}, \end{aligned} \quad (10)$$

$$F_s^{in} \equiv F_0^{in} \prod_{j=1}^s g(x_j)$$

Formulae (6)-(7) and (10) give explicit formal series expansions of non-equilibrium (time-dependent) DF in respect to mean gas density.

### III. CUMULANT DISTRIBUTION FUNCTIONS AND DYNAMICAL VIRIAL RELATIONS

In addition to the DF  $F_s(t) = F_s(t, R, V, x_1 \dots x_s)$ , let us consider functions  $C_s(t) = C_s(t, R, V, x_1 \dots x_s)$  defined by  $C_0 \equiv F_0$  and, at  $s > 0$ , the series as follow:

$$\begin{aligned} C_s(t) &= e^{L_0 t} \prod_{j=1}^s \circ[e^{L_j t} - 1] g(x_j) \left\{ 1 + \sum_{k=1}^{\infty} \frac{n^k}{k!} \prod_{j=s+1}^{s+k} \int_j \circ[e^{L_j t} - 1] g(x_j) \right\} F_0^{in} = \\ &= \sum_{k=0}^{\infty} \frac{n^k}{k!} \int_1 \dots \int_k e^{L_0 t} \prod_{j=1}^{s+k} \circ[e^{L_j t} - 1] g(x_j) F_0^{in} \end{aligned} \quad (11)$$

(at  $k = 0$ , of course, there is no integration).

From this definition it is clear that, first,  $C_s(t = 0) = 0$  at  $s > 0$ .

Second,

$$\begin{aligned} F_1(x_1) &= F_0 g(x_1) + C_1(x_1), \\ F_2(x_1, x_2) &= F_0 g(x_1) g(x_2) + C_1(x_1) g(x_2) + g(x_1) C_1(x_2) + C_2(x_1, x_2), \end{aligned} \quad (12)$$

and so on, where for simplicity only atoms' arguments are exposed. Hence,  $C_s$  represent irreducible  $(s + 1)$ -order correlations between BP and  $s$  atoms and can be named "cumulant functions" (CF).

Third, considering them as functions of the mean gas density too,  $C_s = C_s(t, R, V, x_1 \dots x_s; n)$  (and correspondingly  $F_s = F_s(t, R, V, x_1 \dots x_s; n)$ ), we can write

$$\frac{\partial C_s}{\partial n} = \int_{s+1} C_{s+1} \quad (13)$$

That are the "virial relations" which for the first time were found in an original way in [6, 7] for BP in (generally non-ideal and dense) fluids and then, in [9] and [1-3], derived directly from the BBGKY equations (in some of these references the CFs were designated as  $V_s$ ). In essence, more reasonable name for such kind of results may be "dynamical virial relations" (DVR) [5].

### IV. CONDITIONAL PROBABILITIES AND AVERAGES, AND DVR IN THEIR TERMS

The DVR establish important connections between density dependence (and hence time and space dependence) of the BP's probability distribution,  $F_0$ , and degree and character of BP-gas statistical correlations. The first of relations (13) already was carefully discussed in [6, 7], [9], [1-4], but here we shall refresh it and make more transparent by exploiting the useful concepts of conditional probabilities and conditional averages.

Namely, let us introduce conditional two-particle DF:

$$\frac{F_1(t, R, V, x; n)}{F_0(t, R, V; n)} = \frac{\bar{n}(t, x | R, V; n)}{n}, \quad (14)$$

where  $\bar{n}(t, x | R, V; n) = \bar{n}(t, \rho, v | R, V; n)$  is conditional mean value of instant local density (concentration) of atoms in the  $\mu$ -space under given position and velocity of BP. That is

$$\bar{n}(t, x | R, V; n) = \langle \tilde{n}(t, x) \rangle_{R, V, n} \quad (15)$$

with

$$\tilde{n}(t, x) = \sum_j \delta(x - x_j(t)) = \quad (16)$$

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$$= \sum_j \delta(\rho - (r_j(t) - R(t))) \delta(v - v_j(t))$$

and  $r_j(t)$ ,  $v_j(t)$ ,  $R(t)$ ,  $V(t)$  being instant values of the system's variables. The condition is reflected by the subscript of angle brackets which in turn symbolize, as usually, averaging over given statistical ensemble (determined by  $F_s^{in}$ ).

In terms of conditional statistical characteristics the first of DVR (13), after its multiplication by  $n$ , clearly takes form

$$\begin{aligned} \frac{\partial \ln F_0(t, R, V; n)}{\partial \ln n} &= \\ &= \int [\bar{n}(t, x | R, V; n) - n g(x)] dx = \\ &= \int [\bar{n}(t, \rho | R, V; n) - n E(\rho)] d^3 \rho, \end{aligned} \quad (17)$$

where we introduced also instant local gas density in configurational space,

$$\tilde{n}(t, \rho) = \int \tilde{n}(t, x) d^3 v = \sum_j \delta(\rho - \rho_j(t)), \quad (18)$$

and  $\bar{n}(t, \rho | R, V, n) = \langle \tilde{n}(t, \rho) \rangle_{R, V, n}$  as its conditional ensemble average value.

If we are interested mainly in spatial dependence of  $F_0 = C_0$ , i.e. in the BP's "diffusion law"

$$W(t, R; n) = \int C_0(t, R, V; n) d^3V,$$

then, evidently, instead of (17) we can write [10]

$$\begin{aligned} \frac{\partial \ln W(t, R; n)}{\partial \ln n} &= \\ &= \int [\bar{n}(t, \rho | R; n) - nE(\rho)] d^3\rho = \\ &= \overline{\Delta N}(t | R, n), \end{aligned} \quad (19)$$

with  $\bar{n}(t, \rho | R; n) = \langle \tilde{n}(t, \rho) \rangle_{R, n}$  being conditional mean value of instant gas density at distance  $\rho$  from BP under given BP's position, and  $\overline{\Delta N}(t | R, n)$  corresponding conditional mean change of total number of atoms in BP's surroundings.

Notice that the factor  $nE(\rho)$  is nothing but value of the  $\bar{n}(t, \rho | R; n)$  under complete statistical equilibrium, when there are no statistical correlations between atoms and BP except those coming from their direct dynamic interaction. Therefore, integral in (19),  $\overline{\Delta N}(t | R, n)$ , characterizes specifically non-equilibrium "excess" ("historical" [2]) BP-gas correlations.

## V. DIFFUSION LAW AND FIGHT OF INTUITIONS

Let us consider the BP's diffusion law,  $W(t, R; n)$ , assuming that (i) the BP-atom interaction potential is repulsive and short-range, (ii) the external force is absent,  $f = 0$ , i.e. our system all time stays in equilibrium, and (iii)  $t \gg \tau$ , where  $\tau$  is BP's mean free-flight time (or velocity relaxation time),  $\tau \sim (\lambda/V_0)\sqrt{1 + M/m}$ , with  $\lambda$  being BP's mean free path and  $V_0 = \sqrt{T/M}$  characteristic thermal velocity. According to standard reasonings of gas kinetics and probability theory, firstly,  $\lambda = (\pi a^2 n)^{-1}$  with  $a$  denoting characteristic radius of BP-atom interaction. Secondly,  $W(t, R; n)$  has Gaussian long-time asymptotic,

$$W(t, R; n) \rightarrow W_D^{(G)}(t, R) = \frac{\exp(-R^2/4Dt)}{(4\pi Dt)^{3/2}}, \quad (20)$$

where  $D = D(n)$  is BP's diffusivity,  $D(n) \sim V_0^2 \tau \sim V_0 \lambda \sqrt{1 + M/m} \propto 1/n$  for not too dense gas (at  $4\pi a^3 n/3 \lesssim 1$ ).

This asymptotic expresses the celebrated Bernoulli's "law of large numbers" [11] and is an integral part of common intuition cultivated by probability-theoretical way of thinking in statistical mechanics. However, it never was deduced from rigorous statistical mechanics in itself, without "art of conjectures" (see comments and references in [2, 3, 5, 6, 12–14]). Now, let us combine it with rigorous relation (19) and with the inverse proportionality  $D(n) \propto 1/n$ . This yields

$$\frac{\partial \ln W_D^{(G)}(t, R; n)}{\partial \ln n} = \frac{3}{2} - \frac{R^2}{4Dt} = \overline{\Delta N}(t | R, n), \quad (21)$$

which, in turn, implies that  $\overline{\Delta N}(t | R, n)$  can take arbitrary large negative values. In other words, even in spite of equilibrium nature of the BP's diffusion, statistical correlations between gas and BP can involve arbitrary many atoms.

This conclusion, however, is in contradiction to another common intuitive notion. Namely, that of Boltzmannian "molecular chaos" which usually serves as logical reason of the "law of large numbers". Thus, the DVR visually reveal falsity of both these notions.

To avoid the contradiction, we should refuse hypothesis that rigorous statistical mechanics always allows realization of "molecular chaos" and the "law of large numbers" in transport phenomena. And, hence, we should accept profound conjecture that BP-gas correlations have substantial but bounded value. That is the quantity  $\overline{\Delta N}(t | R, n)$ , - which can be named e.g. "correlation number", - satisfies

$$-\Delta N_- \leq \overline{\Delta N}(t | R, n) \leq \Delta N_+, \quad (22)$$

where  $\Delta N_-$  and  $\Delta N_+$  are positive quantities independent (under long-range asymptotic) on  $R$  and  $t$  and, expectedly (at  $a^3 n \ll 1$ ), also on  $n$ .

This means [2, 6, 7] that instead of (20) we have to write, asymptotically,

$$W(t, R; n) \rightarrow \frac{\Psi(R^2/4Dt)}{(4\pi Dt)^{3/2}} \Xi(R^2/V_0^2 t^2) \quad (23)$$

with  $D = D(n) \propto 1/n$ , where, because of (19) and (22), function  $\Psi(z)$  possesses power-law tail:

$$\Psi(z) \propto \frac{1}{z^\alpha} \quad (z \gg 1), \quad \alpha = \frac{3}{2} + \Delta N_-, \quad (24)$$

and  $\Xi(0) = 1$ . The cut-off function  $\Xi(\cdot)$  (fast decreasing at infinity) can be omitted except when calculating higher-order statistical moments of  $R$ . Since at that, evidently,  $\Delta N_+ = \max_z \partial \ln W / \partial \ln n = 3/2$ , the exponent  $\alpha$  can be expressed as  $\alpha = \Delta N_+ + \Delta N_-$ . Explicit example of such (realistic) "diffusion law", - for probe atom of slightly non-ideal gas in the role of BP, - with the characteristic "correlation number"  $\Delta N_- = 2$ , is presented in [14]. Thus, probabilities of large deviations of BP's path from its typical values ( $|R| \sim \sqrt{6Dt}$ ) are giant as compared with predictions of the (idealistic) Gaussian law.

In [2, 6, 7], these consequences of the first of DVR (13) were considered in different fashion, in terms of characteristic volume,  $\Omega_c$ , occupied by BP-gas correlations in the  $\rho$ -space. It appears in the above formulae if we notice [10] that, due to non-negativity of  $\bar{n}(t, \rho | R, n)$ , equality (19) implies inequality

$$\frac{\partial \ln W(t, R; n)}{\partial \ln n} \gtrsim -n\Omega_c \quad (25)$$

(we neglect contributions  $\sim a^3$  in comparison with  $\Omega_c$ ). This coincides with (22) at  $\Omega_c = \Delta N_-/n$ . An unambiguous formal definition of  $\Omega_c$  was done in [2, 6, 7].

The asymptotic (23)-(24) means that BP has no *a priori* certain diffusivity. Instead, a variety of possible BP's trajectories is characterized by some effective distribution,  $U(D; t, n)$ , of its diffusivity, so that

$$W(t, R; n) \rightarrow \int_0^\infty W_{D'}^{(G)}(t, R) U(D'; t, n) dD' \quad (26)$$

According to (23) and (24), the distribution must have definite power-law tail and thus look e.g. like

$$U(D; t, n) \propto \frac{D_0^{\Delta N_-}}{D^{\Delta N_- + 1}} \exp\left(-\frac{D_0}{D}\right) \Xi\left(\frac{D}{V_0^2 t}\right) \quad (27)$$

with  $D_0 = D_0(n) \propto 1/n$  being characteristic diffusivity scale and  $\Xi(\cdot)$  nearly the same cut-off function as in (23). Correspondingly, in (23)

$$\Psi(z) = \frac{\Gamma(\alpha)}{\Gamma(\alpha - 3/2)} \cdot \frac{1}{(1+z)^\alpha} \quad (28)$$

with  $\alpha = \Delta N_- + 3/2$ . Coefficient  $\Gamma(\alpha)/\Gamma(\alpha - 3/2)$  is normalizing factor ensuring that (asymptotically)  $\int W(t, R; n) d^3 R = 1$ . This is direct analogue of distributions found in [14] (for probe atom of weakly non-ideal gas) and in [15] (for BP different from non-ideal gas atoms [16]) in the “collisional approximation” of BBGKY equations [12–15].

According to the universal “generalized fluctuation-dissipation relations” (see e.g. [10] and [12, 13, 17] and references therein), the representation (26)-(27), with

$$W_D^{(G)}(t, R) = \frac{\exp[-(R - Df/T)^2/4Dt]}{(4\pi Dt)^{3/2}} \quad (29)$$

in place of (20), is valid also for non-equilibrium Brownian motion under non-zero external force,  $f \neq 0$ , at least for sufficiently small one,  $f\lambda \ll T$ .

The resulting distribution predicts and describes 1/f-type fluctuations of BP's mobility  $\mu = D/T$ , as well as at  $f = 0$  similar 1/f-type fluctuations of BP's diffusivity [2, 4, 6, 7, 10, 12–14, 17–24], thus confirming logics of the Krylov's “art of conjectures” [25].

At  $D_0(f/T)^2 t \gg 1$  (when drift contribution to BP's path  $R(t)$  exceeds diffusive contribution) this mobility/diffusivity 1/f-noise visually manifests itself in probability distribution of  $R(t)$ 's projection onto  $f$ 's direction [6]: according to (26) and (44), its shape nearly reproduces that of  $U(D; t, n)$  (analogous distributions of charge carriers' mobilities in electronics were detected by time-of-flight measurements [22]).

## VI. HIGHER-ORDER CONDITIONAL PROBABILITIES AND VIRIAL RELATIONS

It is not hard to see that expansions (10) and (11) or, equivalently, formulae (12) together with the DVR (13)

imply relations

$$\frac{\partial F_s}{\partial n} = \int_{s+1} [F_{s+1} - g(x_{s+1}) F_s] \quad (30)$$

After dividing by  $F_s$  and multiplying by  $n$  this yields many-particle analogue of (17),

$$\begin{aligned} \frac{\partial \ln F_s}{\partial \ln n} &= \overline{\Delta N}_s(t|R, V, x^{(s)}, n) = \\ &= \int [\bar{n}(t, x|R, V, x^{(s)}) - g(x)n] dx \end{aligned} \quad (31)$$

with  $x^{(s)} = \{x_1 \dots x_s\}$  and  $\bar{n}(t, x|R, V, x^{(s)}, n)$  being conditional average of  $\tilde{n}(t, x)$  under condition that BP is in given state and, besides, some  $s$  atoms already occupy  $s$  exactly known states.

Then, introducing many-particle DF in configurational space,

$$W_s(t, R, \rho^{(s)}; n) = \int F_s d^3 V d^3 v_1 \dots d^3 v_s,$$

where  $\rho^{(s)} = \{\rho_1 \dots \rho_s\}$ , one can transform (30)-(31) to

$$\begin{aligned} \frac{\partial \ln W_s}{\partial \ln n} &= \overline{\Delta N}_s(t|R, \rho^{(s)}, n) = \\ &= \int [\bar{n}(t, \rho|R, \rho^{(s)}, n) - E(\rho)n] d^3 \rho \end{aligned} \quad (32)$$

with  $\bar{n}(t, \rho|R, \rho^{(s)}, n) = \langle \tilde{n}(t, \rho) \rangle_{R, \rho^{(s)}, n}$  representing average under condition that  $s$  atoms are known already to be at given distances from BP.

To interpret these formulae correctly, recall that, - by statistical definition of DFs  $F_s$  (see also [8] and below), - different arguments  $x_j$  of  $F_s$ , relate to different atoms. Therefore,  $s$  atoms entering into the conditions in fact do not enter into  $\tilde{n}(t, x)$  and  $\bar{n}(t, \rho)$ . As the consequence, a contribution they give to  $\overline{\Delta N}(t|R, n)$  in (19) is absent in  $\overline{\Delta N}_s(t|R, \rho^{(s)}, n)$  in (32), so that we can write

$$\overline{\Delta N}_s(t|R, \rho^{(s)}, n) \geq \overline{\Delta N}(t|R, n) - s \quad (33)$$

At that, of course,  $\overline{\Delta N}_s(t|R, \rho^{(s)}, n) \rightarrow \overline{\Delta N}(t|R, n)$  when points  $\rho^{(s)}$  are far from the “correlation volume”  $\Omega_c$ , i.e.  $\rho^{(s)} \rightarrow \infty$ , and equality in (33) can be achieved only at small enough  $\rho^{(s)}$  belonging to  $\Omega_c$ .

Together with these reasonings, formulae (32), (33) and (22) naturally do prompt that for  $s > 0$ , - in addition to (22), (23) and (28), - the following asymptotical estimates take place (at  $f = 0$ ):

$$\min \overline{\Delta N}_s(t|R, \rho^{(s)}, n) = -\Delta N_- - s, \quad (34)$$

$$\overline{W}_s(t, R; n) \rightarrow \frac{\Psi_s(R^2/4Dt)}{(4\pi Dt)^{3/2}} \Xi(R^2/V_0^2 t^2), \quad (35)$$

$$\begin{aligned} \Psi_s(z) &= \frac{\Gamma(\alpha_s)}{\Gamma(\alpha_s - 3/2)(1+z)^{\alpha_s}} \propto \frac{\Psi(z)}{(1+z)^s}, \quad (36) \\ \alpha_s &= \Delta N_- + s + 3/2, \quad (37) \end{aligned}$$

where the minimum is taken over  $R$  and  $\rho^{(s)}$ , and  $\overline{W}_s(t, R; n)$  means result of suitable smoothing of

$W_s(t, R, \rho^{(s)}; n)$  over small enough  $\rho^{(s)}$  from the “correlation volume”. At that,  $\int \bar{W}_s(t, R; n) d^3 R = 1$ , as the above basic definition of  $W_s$  does require.

Thus, the sequence of functions  $\bar{W}_s(t, R; n)$  qualitatively coincides with sequence  $\bar{W}_s(t, R)/(1 + sm/M)$  from [15] (see also [6]), and coincidence would be also quantitative if the “correlation number”  $\Delta N_-$  was equal to  $1 + M/m$  (see below). This observation confirms that exact DVR (30)-(32) and the “collisional approximation” [12–15] are rather close approaches.

One can notice that the sequence  $\bar{W}_s = \bar{W}_s(t, R; n)$  satisfies (at  $D \propto 1/n$ ) simple recurrent relations

$$\bar{W}_{s+1} = \left[ 1 + \frac{n}{\Delta N_- + s} \frac{\partial}{\partial n} \right] \bar{W}_s \quad (38)$$

(more generally,  $n \partial/\partial n$  may be replaced by  $-D \partial/\partial D$ ).

Iterating them, after some combinatoric algebra one can obtain

$$\begin{aligned} \bar{W}_s &= \prod_{k=0}^{s-1} \frac{\Delta N_- + s + n \partial/\partial n}{\Delta N_- + s} W_0 = \\ &= \sum_{k=0}^s \binom{s}{k} \frac{\Gamma(\Delta N_-)}{\Gamma(\Delta N_- + k)} n^k \frac{\partial^k}{\partial n^k} W_0 \end{aligned} \quad (39)$$

Right-hand side here is mere result of “normal ordering” of multiplication and differentiation operators  $n$  and  $\partial/\partial n$  from left side.

At  $f \neq 0$  (in the linear drift response regime), correspondingly,

$$\bar{W}_s \rightarrow \int_0^\infty W_{D'}^{(G)}(t, R - D' f t / T) U_s(D'; t, n) dD', \quad (40)$$

$$U_s(D; t, n) = \frac{D_0^{\Delta N_- + s}}{\Gamma(\Delta N_- + s) D^{\Delta N_- + 1 + s}} \exp\left(-\frac{D_0}{D}\right) \Xi\left(\frac{D}{V_0^2 t}\right), \quad (41)$$

where effective diffusivity distributions  $U_s$  obey recurrent relations

$$U_{s+1}(D; t, n) = \left[ 1 + \frac{n}{\Delta N_- + s} \frac{\partial}{\partial n} \right] U_s(D; t, n) \quad (42)$$

at  $D_0 \propto 1/n$ .

## VII. GENERATING FUNCTIONALS AND VIRIAL RELATIONS

For many purposes it is convenient to accumulate all DFs in a single generating functional (GF),

$$\mathcal{F}\{t, R, V, \psi; n\} = F_0 + \sum_{s=1}^{\infty} \frac{n^s}{s!} \int_1 \dots \int_s F_s \psi(x_1) \dots \psi(x_s) \quad (44)$$

with  $\psi(x)$  being formally arbitrary probe function. Following the original general Bogolyubov’s construction of such functionals in [8] (where probe function  $u(x) = n\psi(x)$  was used instead of  $\psi(x)$ ), we can introduce our one as thermodynamic limit of

$$\begin{aligned} \mathcal{F}_N\{t, R, V, \psi; n\} &= F_0 + \sum_{s=1}^N \frac{N!}{s!(N-s)!\Omega^s} \int_1 \dots \int_s F_s \psi(x_1) \dots \psi(x_s) \equiv \\ &\equiv \int_1 \dots \int_N D_N(t) \prod_{j=1}^N [1 + \psi(x_j)] = \int_1 \dots \int_N \exp \left\{ \sum_{j=1}^N \ln [1 + \psi(x_j)] \right\} D_N(t) = \\ &= \int_1 \dots \int_N \exp \left\{ \int \tilde{n}(t, x) \ln [1 + \psi(x)] dx \right\} D_N(t), \end{aligned}$$

where  $\Omega = N/n$ , and we involved the “microscopic gas density”  $\tilde{n}(t, x) = \sum_{j=1}^N \delta(x - x_j(t))$  whose statistics is determined by the total DF  $D_N(t)$  in turn determined by (1) and (3). The latter expressions highlight statistical meaning of the functional (44),  $\mathcal{F} = \lim \mathcal{F}_N$ , allowing us to write [4]:

$$\mathcal{F}\{t, R, V, \psi; n\} = \left\langle \delta(R - R(t)) \delta(V - V(t)) \exp \left\{ \int \tilde{n}(t, x) \ln [1 + \psi(x)] dx \right\} \right\rangle_n =$$

$$= F_0(t, R, V; n) \left\langle \exp \left\{ \int \tilde{n}(t, x) \ln [1 + \psi(x)] dx \right\} \right\rangle_{R, V, n} \quad (45)$$

Here, as above,  $\langle \dots \rangle_{R, V, n}$  is symbol of conditional averaging under given BP's variables, so that the latter angle brackets represent conditional characteristic functional of random field  $\tilde{n}(t, x)$ , with  $\xi(x) = \ln [1 + \psi(x)]$  in the role of probe function.

Next, introduce, in full analogy with (44), GF of the CFs (11):

$$\mathcal{C}\{t, R, V, \psi; n\} = C_0 + \sum_{s=1}^{\infty} \frac{n^s}{s!} \int_1 \dots \int_s C_s \psi(x_1) \dots \psi(x_s) = \mathcal{P}\{t, R, V, (1 + \psi) n\}, \quad (46)$$

$$\mathcal{P}\{t, R, V, \chi\} \equiv \sum_{s=0}^{\infty} \frac{1}{s!} \left\{ \int_1 \dots \int_s \chi(x_1) \dots \chi(x_s) e^{L_0 t} \prod_{j=1}^s \circ [e^{L_j t} - 1] g(x_j) \right\} F_0^{in}(R, V) \quad (47)$$

The latter equality in (46) directly follows from CF's definitions (11), with functional  $\mathcal{P}\{t, R, V, \chi\}$  representing unified "propagator" for all CF's. In view of (12),

$$\mathcal{F}\{t, R, V, \psi; n\} = \mathcal{C}\{t, R, V, \psi; n\} \exp \left\{ n \int \psi(x) g(x) dx \right\} \quad (48)$$

Since, again by the CFs definition,  $C_s(t=0) = 0$  at  $s > 0$  and therefore  $\mathcal{C}\{t=0, R, V, \psi; n\} = F_0^{in}(R, V)$ , one can see that the exponential in (48) is conditional characteristic functional of thermodynamically equilibrium gas:

$$\frac{\mathcal{F}\{t=0, R, V, \psi; n\}}{F_0^{in}(R, V)} = \exp \left\{ n \int \psi(x) g(x) dx \right\} = \left\langle \exp \left\{ \int \tilde{n}(t, x) \ln [1 + \psi(x)] dx \right\} \right\rangle_{R, V, n}^{eq} \quad (49)$$

Factual independence of this functional on  $\{R, V\}$  just reflects the gas' equilibrium, which is indicated by superscript "eq". The change of variable  $\psi(x) = \exp [\xi(x)] - 1$  transforms (49) into

$$\exp \left\{ n \int g(x) [e^{\xi(x)} - 1] dx \right\} = \left\langle \exp \left\{ \int \tilde{n}(t, x) \xi(x) dx \right\} \right\rangle_{R, V, n}^{eq}, \quad (50)$$

which shows that corresponding statistics of random disposition of gas atoms in  $\mu$ -space is trivial Poissonian.

However, the equilibrium of gas itself does not mean that of the whole system, if  $F_0^{in}(R, V)$  differs from  $\Omega^{-1} G_M(V)$ . Then at  $t > 0$  the above mentioned excess "historical" correlations between gas and BP will appear to be accumulated by GF (46). For the first time these correlations, in their connections with BP's diffusion law, were considered in [26, 27]. In our present case of BP in ideal gas, these connections, expressed by DVRs (13), together form generating DVR [1, 2, 4] (quite obvious from (47))

$$\mathcal{C}\{t, R, V, \sigma + \psi; n\} = \mathcal{C}\{t, R, V, \psi/(1 + \sigma); (1 + \sigma)n\}, \quad (51)$$

where  $\sigma = \text{const}$  is independent on  $x$ .

## VIII. DIFFUSION LAW AND ACCOMPANYING GAS STATISTICS

Combining the generating virial relation (51) with (45) and (48), we can write

$$\begin{aligned} F_0(t, R, V; n) \frac{\left\langle \exp \left\{ \int \tilde{n}(t, x) \ln [1 + \sigma + \psi(x)] dx \right\} \right\rangle_{R, V, n}}{\exp \left\{ n \int \sigma g(x) dx \right\}} = \\ = F_0(t, R, V; (1 + \sigma)n) \left\langle \exp \left\{ \int \tilde{n}(t, x) \ln [1 + \psi(x)/(1 + \sigma)] dx \right\} \right\rangle_{R, V, (1 + \sigma)n} \end{aligned} \quad (52)$$

As the consequence, after special choice  $\psi(x) = \phi(\rho)$  and integration over  $V$ , we have

$$\begin{aligned} W(t, R; n) \frac{\left\langle \exp \left\{ \int \tilde{n}(t, \rho) \ln [1 + \sigma + \phi(\rho)] d^3 \rho \right\} \right\rangle_{R, n}}{\exp \left\{ n \int \sigma E(\rho) d^3 \rho \right\}} = \\ = W(t, R; (1 + \sigma)n) \left\langle \exp \left\{ \int \tilde{n}(t, \rho) \ln [1 + \phi(\rho)/(1 + \sigma)] d^3 \rho \right\} \right\rangle_{R, (1 + \sigma)n} \end{aligned} \quad (53)$$

This generating DVR directly connects the diffusion law  $W(t, R; n) = W_0(t, R; n) = \int F_0(t, R, V; n) d^3V$  with gas statistics in configurational space as described by one more GF

$$\begin{aligned} \mathcal{W}\{t, R, \phi; n\} &= W_0 + \sum_{s=1}^{\infty} \frac{n^s}{s!} \int_1 \dots \int_s W_s \phi(\rho_1) \dots \phi(\rho_s) = \\ &= W_0(t, R; n) \left\langle \exp \left\{ \int \tilde{n}(t, \rho) \ln [1 + \phi(\rho)] d^3\rho \right\} \right\rangle_{R, n}, \end{aligned} \quad (54)$$

where now  $\int_j \dots = \int \dots d^3\rho_j$ . Clearly, the integrals in both numerator and denominator on the left in (52) and (53) are formally diverging at  $\sigma \neq 0$ , but the divergencies definitely compensate one another, due to equalities (49)-(50), since at  $\rho \rightarrow \infty$  random fields  $\tilde{n}(t, x)$  and  $\tilde{n}(t, \rho)$  behave like equilibrium Poissonian ones.

Because of arbitrariness of  $\sigma$  and  $\psi(x)$  or  $\phi(\rho)$ , each of relations (52) and (53) produces two independent relations. Namely, for example, (53) yields

$$\frac{W(t, R; (1 + \sigma)n)}{W(t, R; n)} = \left\langle \exp \left\{ \int [\tilde{n}(t, \rho) \ln(1 + \sigma) - n E(\rho) \sigma] d^3\rho \right\} \right\rangle_{R, n}, \quad (55)$$

or, writing  $\sigma = \exp(\xi) - 1$ ,

$$\frac{W(t, R; e^\xi n)}{W(t, R; n)} = \frac{\langle \exp \{ \xi \int \tilde{n}(t, \rho) d^3\rho \} \rangle_{R, n}}{\langle \exp \{ \xi \int \tilde{n}(t, \rho) d^3\rho \} \rangle_n^{eq}} \quad (56)$$

And, taking  $\phi(\rho) = (1 + \sigma) [\exp(\varphi(\rho)) - 1] = e^\xi [\exp(\varphi(\rho)) - 1]$ ,

$$\frac{\langle \exp \{ \int \tilde{n}(t, \rho) [\xi + \varphi(\rho)] d^3\rho \} \rangle_{R, n}}{\langle \exp \{ \int \tilde{n}(t, \rho) \xi d^3\rho \} \rangle_{R, n}} = \left\langle \exp \left\{ \int \tilde{n}(t, \rho) \varphi(\rho) d^3\rho \right\} \right\rangle_{R, e^\xi n} \quad (57)$$

The first of these three equalities is the same as

$$W(t, R; (1 + \sigma)n) = \mathcal{C}\{t, R, \sigma; n\}, \quad (58)$$

which follows from (51) at  $\psi(x) = 0$  after integration over BP's velocity, with GF

$$\begin{aligned} \mathcal{C}\{t, R, \phi; n\} &\equiv \int \mathcal{C}\{t, R, V, \psi(x) = \phi(\rho); n\} d^3V = \\ &= C_0(t, R; n) + \sum_{s=1}^{\infty} \frac{n^s}{s!} \int C_s(t, R, \rho^{(s)}; n) \phi(\rho_1) \dots \phi(\rho_s) d\rho^{(s)} = \frac{\mathcal{W}\{t, R, \phi; n\}}{\exp[n \int E(\rho) \phi(\rho) d^3\rho]} \end{aligned} \quad (59)$$

of CFs integrated over all velocities,  $C_s(t, R, \rho^{(s)}; n) \equiv \int \int C_s dv^{(s)} d^3V$ .

Now, let us discuss the above approximate asymptotic expressions for  $W(t, R; n)$  at  $f = 0$  in the light of the exact relations (55)-(56) or (58)) and (57).

In the Gaussian model (20), with  $D(n) \propto 1/n$ , and in our approximation (23) left side of (55) and (56) looks as

$$\begin{aligned} \frac{W_{D((1+\sigma)n)}^{(G)}(t, R)}{W_{D(n)}^{(G)}(t, R)} &= (1 + \sigma)^{3/2} \exp(-\sigma z) = \\ &= \exp \left[ \frac{3\xi}{2} - z(e^\xi - 1) \right] = \frac{W_{D(\exp(\xi)n)}^{(G)}(t, R)}{W_{D(n)}^{(G)}(t, R)}, \end{aligned} \quad (60)$$

$$\begin{aligned} \frac{W(t, R; (1 + \sigma)n)}{W(t, R; n)} &= \frac{(1 + \sigma)^{3/2}}{(1 + \sigma z / (1 + z))^{\Delta N_- + 3/2}} = \\ &= \exp \left\{ \frac{3\xi}{2} - \left( \Delta N_- + \frac{3}{2} \right) \ln \left[ 1 + \frac{z}{1 + z} (e^\xi - 1) \right] \right\} = \frac{W(t, R; e^\xi n)}{W(t, R; n)}, \end{aligned} \quad (61)$$

where  $z = R^2/4D(n)t \propto n$  and  $\sigma = \exp \xi - 1$ .

At  $z = 0$  both these expressions reduce to  $(1 + \sigma)^{3/2} =$



$\exp[(3/2)\xi]$ . From viewpoint of right-hand side of (55)-(56) it says that the integral  $\int \tilde{n}(t, \rho) d^3\rho \equiv \tilde{N}(t)$ , - representing number of atoms in some relevant volume around BP, - consists of non-random constant  $3/2$  and random component which behaves exactly like  $\tilde{N}(t)$  in equilibrium, with the same Poissonian statistics. Symbolically,  $\tilde{N}(t) = 3/2 + \tilde{N}_{eq}(t)$ .

Literal interpretation of this statement would mean that, strangely,  $\tilde{N}(t)$  takes non-integer values. However, such interpretation would be ill-advised, since the proportionality  $D(n) \propto 1/n$ , - which just causes factor  $(1 + \sigma)^{3/2} = \exp[(3/2)\xi]$  (through  $W(t, 0; n) \propto (4\pi D(n)t)^{-3/2}$ ), - is approximate and applicable only when

$$(\pi a^2 V_0 t)^{-1} \ll n \ll (4\pi a^3/3)^{-1}$$

and, besides,  $(1 + \sigma)n = \exp(\xi)n$  also lies within these bounds. What we can state, is that contribution  $3/2$  in  $\tilde{N}(t) = 3/2 + \tilde{N}_{eq}(t)$  indicates BP-atoms statistical correlations produced, of course, by (actual or virtual) collisions of atoms with BP. At  $z = 0$ , in that way, that are naturally positive correlations: if in spite of  $t \gg \tau$  BP has not gone away far from its start position, then number of atoms in its surroundings on average is greater than under initial equilibrium (for fixed BP), so that

$$\overline{\Delta N}(t|0, n) = \langle \tilde{N}(t) \rangle_{R=0, n} - \langle \tilde{N}_{eq} \rangle_n = 3/2 \quad (62)$$

with  $\langle \tilde{N}_{eq} \rangle_n = \langle \tilde{N}(t) \rangle_n^{eq}$ .

At finite  $z > 0$ , obviously, in both the cases (60) and (61)  $\overline{\Delta N}(t|R, n)$  decreases and becomes negative at  $z > 3/2$  and  $z > 3/2\Delta N_-$ , respectively, again in agreement with intuition: the greater is current BP's distance from its start point, the smaller is number of atoms around it, i.e. "number of obstacles" to its flight, in comparison with equilibrium. But numerical and statistical characteristics of this atoms' "shortage" in cases (60) and (61) are qualitatively different.

Namely, the Gaussian model, according to (60 or (21), must be associated with infinitely growing shortage,  $\overline{\Delta N}(t|R, n) = 3/2 - z$ . Thus, if  $|R| \sim V_0 t$  then the shortage is of order of  $z \sim t/\tau$ , i.e. as large as a number of missed BP-atom collisions, as if long ago missed atoms somehow determined current shortage. Indeed, this is physically rather absurd picture!

Another picture, which arises under our approximation, looks much more likely. Here, according to (22) and (61), mean shortage is bounded,

$$\overline{\Delta N} = \frac{3}{2} - \left[ \Delta N_- + \frac{3}{2} \right] \frac{z}{1+z} \rightarrow -\Delta N_- \quad (63)$$

Besides, it obeys essentially non-Poissonian statistics, which means presence of statistical correlations between composing atoms. One may describe this statistics by treating the "microscopic gas density"  $\tilde{n}(t, \rho)$  as "twice stochastic" point field ("spatial random point process"),

i.e. Poissonian field with fluctuating intensity. Then, applying in (61) integral expansion

$$\begin{aligned} \exp \left\{ - \left( \Delta N_- + \frac{3}{2} \right) \ln \left[ 1 + \frac{z}{1+z} (e^\xi - 1) \right] \right\} = \\ = \int_0^\infty \exp \left[ -u \frac{z}{1+z} (e^\xi - 1) \right] \times \\ \times \frac{u^{\Delta N_- + 1/2} \exp(-u)}{\Gamma(\Delta N_- + 3/2)} du, \quad (64) \end{aligned}$$

we can treat factor

$$\Delta N \equiv 3/2 - uz/(1+z) \quad (65)$$

(with  $u$  obeying the gamma distribution) as fluctuating excess or shortage (dependently on  $\Delta N$ 's sign) of number of atoms in correlation volume near BP. At that, its average value equals to (63) while most probable value,  $\Delta N_{m.p.}(z)$ , is smaller,

$$\Delta N_{m.p.} = \frac{3}{2} - \left[ \Delta N_- + \frac{1}{2} \right] \frac{z}{1+z} \rightarrow 1 - \Delta N_- \quad (66)$$

(since most probable value of  $u$  is  $\Delta N_- + 1/2$ ).

Let us use it for estimation of limits in (63) and (66), that is characteristic correlation number  $\Delta N_-$ . Introduce quantity

$$\Delta M \equiv M + m \Delta N \quad (67)$$

It represents excess (or shortage) of total mass (of BP and atoms) located inside the correlation volume  $\Omega_c$ , in comparison with mean mass  $mn\Omega_c$  of other regions having such volume but not containing BP. Notice, first, that in perfectly equilibrium statistical ensemble, - where BP's position is fully uncertain,  $W(R) = 1/\Omega$ , - the same quantity  $mn\Omega_c$  gives mean mass of arbitrary region with volume  $\Omega$ , even though it may contain BP. Second, since in our ensemble the limit value of  $\Delta N$  at  $z \rightarrow \infty$  appears insensible to  $z$ , it in fact also corresponds to fully uncertain BP's position ("at infinity"). Therefore we can expect that the excess-shortage mass  $\Delta M$  in our ensemble at  $z \rightarrow \infty$  becomes the same as in perfectly equilibrium ensemble, i.e. turns to zero. Then, if addressing this requirement to most probable value of  $\Delta M$ , i.e. identifying  $\Delta N$  in (67) with  $\Delta N_{m.p.}(\infty)$  from (66), we come to equality

$$M + (1 - \Delta N_-)m = 0, \quad (68)$$

which suggests for  $\Delta N_-$  value  $\Delta N_- = 1 + M/m$ .

This value coincides with what was found formally, under the collisional approximation, in [14, 15] for BP in non-ideal gas. Of course, our derivation of (68) is less formally grounded, and factual value of  $\Delta N_-$  may differ from  $1 + M/m$ . Nevertheless, undoubtedly, this result correctly reflects role of mass ratio  $M/m$  in construction of the law of diffusion, and confirms  $\Delta N_-$ 's indifference to gas density.

As the consequence, we can improve estimate of the correlation volume  $\Omega_c$  and make estimate of its analogues for higher-order CFs. With this purpose let us return to formula (39). Due to relations (12) we can write

$$\overline{W}_s = \sum_{k=0}^s \binom{s}{k} \overline{C}_k,$$

where  $\overline{C}_s = \overline{C}_s(t, R; n)$  are CFs smoothed over small enough  $\rho^{(s)}$ . Combining this with (39) and DVR (13), we obtain

$$\overline{C}_s = \frac{\Gamma(\Delta N_-)}{\Gamma(\Delta N_- + s)} n^s \int_1 \dots \int_s C_s \quad (69)$$

The factor before integral here just has meaning of inverse  $3s$ -dimensional characteristic volume occupied by  $(s+1)$ -order irreducible correlation between BP and  $s$  atoms. Thus the  $3s$ -dimensional volume itself is

$$\Omega_{cs} = \frac{\Delta N_- \dots (\Delta N_- + s - 1)}{n^s}, \quad (70)$$

in particular,  $\Omega_c \equiv \Omega_{c1} = \Delta N_- / n$ .

This expression, being supplemented with above estimate  $\Delta N_- = 1 + M/m$ , acquires visual explanation. Namely, at  $M/m \lesssim 1$  we see from (70) that  $\Omega_{cs}^{1/s} \sim ((s+1)!)^{1/s}/n \sim (s+1)/en$ . Hence, 3D correlation volume of a particular BP-atom link (in  $\rho_j$ -space) grows proportionally to  $s$ , that is correlation between BP and one of atoms is mediated and lengthened by all  $s-1$  others. Physically, this means that all they are participants of a same connected cluster of  $s$  (actual or virtual) collisions (or “encounters” [12, 13]), and most long-range contributions to  $\Omega_{cs}^{1/s}$  come from cylinder-like regions (“collision cylinders”) with cross-section  $\sim \pi a^2$  and length  $\sim s\lambda$  (thus, with volume  $\sim s\pi a^2 \lambda = s/n$ ).

If  $M/m \gg 1$ , then formula (70) implies, at not too large  $s$ , value  $\Omega_{cs}^{1/s} \sim \Omega_c \sim M/mn$ . Its approximate independence on  $s$  says about relative weakness of (BP-mediated) inter-atom correlations inside the clusters (if BP was immovable, they would vanish at all).

Physical meaning of the proportionality  $\Omega_c \propto M/m$  at  $M/m \gg 1$  also is quite transparent. Indeed,  $\Omega_c$  is formed by “collision cylinders” with length  $\Lambda$  of order of atom’s flight path during BP’s velocity relaxation time  $\tau$ , i.e.  $\Lambda \sim \tau \sqrt{T/m}$ . At that,  $\tau \sim M\lambda/\sqrt{Tm}$  [28]. This value follows e.g. from phenomenological equation for BP’s momentum relaxation in light dilute gas:

$M\dot{V} \approx -(V/\lambda)\sqrt{Tm}$ . Hence,  $\Lambda \sim (M/m)\lambda$ , thus explaining why  $\Omega_c = \Delta N_- / n \approx \pi a^2 \Lambda \approx M/mn$ .

Above reasonings demonstrate that characteristic “correlation volume” can be thought as a weighted sum (union), or statistical sum, of variously oriented (and may be coupled) “collision cylinders”. That is why volume  $\Omega_c$  is determined by  $1/n$ , but not  $\lambda^3 \gg 1/n$ , although its

greatest linear size is determined by  $\lambda$ . Such construction of the correlations implies strongly non-uniform distribution of “density of correlations” inside  $\Omega_c$ . For instance, - as was suggested already in [27] (and discussed also in [5]), - schematically,  $C_1(t, R, \rho; n)/\overline{C}_1(t, R; n) \sim (a^2/4|\rho|^2) \exp(-|\rho|/\Lambda)$  at  $|\rho| \gtrsim a$ , which reveals hidden motive of relations (69)-(70). At this point, however, we enter to “terra incognita”.

## IX. CONCLUSION

We have tested one more novel and unprejudiced approach to the problem about molecular Brownian particle (BP) in ideal gas, basing on explicit density expansions of (time-depending non-equilibrium) probability distribution functions and on exact dynamical virial relations (DVR) obtained directly from these expansions. Previous approaches were based on the “generalized fluctuation-dissipation relations” (FDR) [6, 7, 27] (about FDR themselves and their other applications see e.g. [10] and references therein), on the BBGKY equations and Bogolyubov’s generating functional equation [1–4, 9, 27], on the “stochastic representation of deterministic interactions” [29] and path integrals [1, 29]. So much attention to seemingly too particular problem was caused by understanding that in fact it is very non-trivial for real “honest” statistical mechanics (SM). Though it is quite trivial for “Boltzmannian version” of SM exploiting “Bernoullian way of thinking”, i.e. belief that many-particle chaos can be divided into “independent” elementary events with strictly certain probabilities. In the framework of this fantasy, long-range statistics of random walk of molecular-size BP does not differ from standard mathematical Brownian motion (diffusive process, Wiener process, etc.), while in real SM one reveals random walk without certain diffusivity and mobility or, in other words, with  $1/f$ -type fluctuations of diffusivity and mobility. This difference, firstly, illustrates Krylov’s statement [25] that the only “elementary events” what generally can be independent and have certain probabilities are whole phase trajectories of one or another many-particle system. Secondly, highlights where one should search for origin of various  $1/f$  noises. They, along with accompanying historical correlations [2], manifest uniqueness of any factual phase trajectory (experiment). Thirdly, the mentioned difference once again shows that “surprises in theoretical physics” do continue, and failure of the “law of conservation of slopiness” [30] (in molecular chaos considerations) supplements their collection. Hence, the problem under our attention is of principal importance.

We developed analysis of our present system in terms of conditional statistical characteristics of microscopic gas density under given BP’s path passed during total observation time. We transformed the DVR into simple and intelligible relations between these gas characteristics and BP’s diffusion law. First of all, principal re-

lation between its scaling exponents in respect to mean gas density and BP's path value, on one hand, and conditional mean number of gas atoms covered by instant statistical correlations with BP, on the other hand. We demonstrated that such relations predict essentially non-Gaussian BP's law of diffusion possessing nearly power-law long tail. Moreover, they, - in combination with natural heuristic reasonings, - allow quantitative estimate of the tail's exponent even without formal summation of

the explicit expansions.

The ancient classical "kinetic theory of gases" is unfamiliar with so remarkable relations, but now gets chance to enhance its "mental outfit" and language and include notion of molecular chaos which produces  $1/f$  noise. Simultaneously, of course, we need in more complete mathematical investigation (if not exact solution) of the problem about BP in ideal gas, along with other problems about spatial-temporal statistics of relaxation and transport processes in many-particle systems.

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